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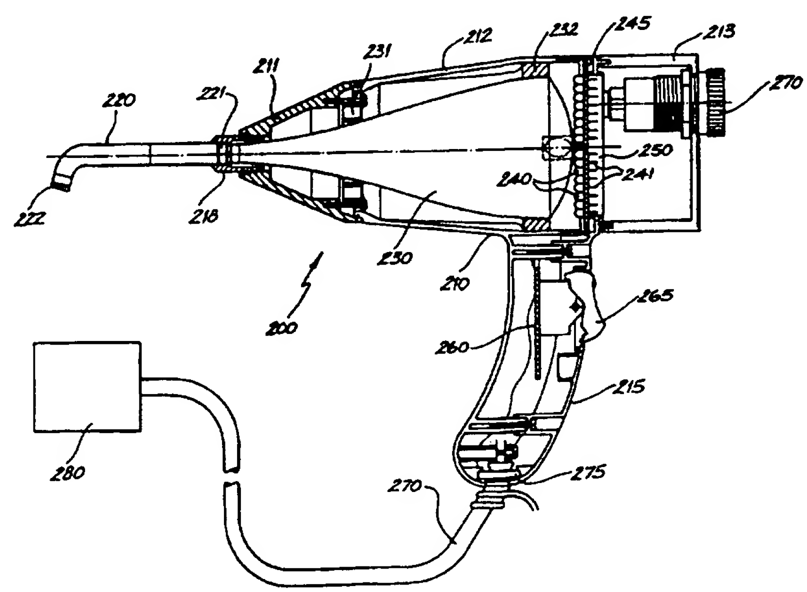

(57) Abstract

There is disclosed a method for initiating the polymerisation of a photopolymerisable dental composition comprising a photoinitiator capable of initiating the polymerisation when irradiated with light having a wavelength between a lower wavelength and an upper wavelength, which method comprises the step of irradiating the composition with light emitted from a light-emitting diode source having an emission wavelength maximum between the lower wavelength and the upper wavelength. There is also disclosed an apparatus for use in the disclosed method, the apparatus comprising a light-emitting diode source (240), a light conduit (220) having a proximal end and a distal end, and condenser means (230) operatively associated with the source and the light conduit for directing light emitted by the source onto the proximal end (221) of the light conduit.

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Apparatus and Method for Polymerising Dental Photopolymerisable Compositions

Technical Field

This invention relates to methods for initiating the photopolymerisation of photopolymerisable compositions, especially for dental use, and to apparatus capable of being used for irradiating a photopolymerisable dental composition with light.

Background Art

As concerns about the use of mercury in dental amalgams continue to grow, dentists are increasingly turning to resins or composites to fill dental cavities. Known resins or composites for dental use contain a photoinitiator which triggers polymerisation when subjected to light with an intensity of 50-500mW cm^{-2}, typically at wavelengths in the region of 400-500 nm.

Existing light sources used in dental applications are based on 150-300 W tungsten-halide lamps, which are high intensity incandescent sources emitting over a range of wavelengths from ultra-violet to infra-red. The wavelengths of light required, usually blue light, are obtained by using filters to block the ultra-violet light, the infra-red or heat radiation and the unwanted visible radiation. Since most of the light from the tungsten-halide lamp is at unwanted wavelengths, this system is necessarily inefficient and normally requires a mains-operated power supply and a cooling fan.

Some disadvantages of these systems currently in use are:

the poor match between the frequencies emitted by a tungsten-halide source, even with filtering, and the absorption spectrum of the photoinitiator in typical photopolymerisable compositions can lead to a less than optimum degree of conversion of the composition in curing methods of the prior art; for example a conversion of only about 65% may be achieved instead of 100% in a given time: such sub-optimal conversion is one source of poor mechanical properties in the cured material;

unwanted infra-red and visible radiation, either alone or in combination with long exposure times, can lead to a higher than desirable rise in the temperature of the dental composite, thus causing thermal stresses in the composite (another source of poor mechanical properties in the cured material) and some patient discomfort;

the output intensity of known tungsten-halide lamps falls in an uncontrolled and usually undetected way over the operating lifetime of the lamp; consequently the dentist either routinely over-exposes in order to attempt to obtain an adequate cure or else uses standard curing times but fails to get a proper cure of the composite;

unwanted ultra-violet radiation presents a hazard to the patient and to the operator and necessitates the use of light absorbing eye shields;

a hand-held unit for directing the filtered light onto the composite in a dental filling must have holes for forced air-cooling and thus cannot be sterilised easily;

the cooling fan is noisy; and

tungsten-halide lamps used in such applications have a useful lifetime only of the order of one hundred hours.

Accordingly there is a need for an improved method of initiating the polymerisation of a photopolymerisable dental composition.

It is an object of the present invention to overcome at least some of the limitations of existing devices for initiating the polymerisation of composites for dental applications.

Summary of the Invention

Surprisingly, it has been discovered by the present inventors that the polymerisation of a photopolymerisable dental composition which comprises a photoinitiator capable of initiating the polymerisation when irradiated with light having a wavelength in a certain range may be initiated with light from a relatively low energy light source, namely a light-emitting diode. For example, it has been discovered that the use of a plurality of light-emitting diodes having an emission wavelength maximum in the range of about 400-500nm provides an effective and hitherto unforeseen method for photoinitiating the polymerisation of such composites which comprise camphorquinone as photoinitiator.

Thus, according to a first embodiment of the present invention there is provided a method for initiating the polymerisation of a photopolymerisable dental composition comprising a photoinitiator capable of initiating said polymerisation when irradiated with light having a wavelength between a lower wavelength and an upper wavelength, which method comprises irradiating said composition with light emitted from a light-emitting diode source having an emission wavelength maximum between said lower wavelength and said upper wavelength.

According to a second embodiment of the present invention there is provided an apparatus for irradiating a photopolymerisable dental composite comprising a light-emitting diode source, a light conduit having a proximal end and a distal end, and condenser means operatively associated with said source and said light conduit for directing light emitted by said source onto said proximal end of said light conduit.

Typically the apparatus of the second embodiment is adapted to be capable of irradiating a photopolymerisable dental composition which comprises a photoinitiator capable of initiating polymerisation of said composition when irradiated with light having a wavelength between a lower wavelength and an upper wavelength, said source having an emission wavelength maximum between said lower wavelength and said upper wavelength.

Thus, according to a third embodiment of the present invention there is provided an apparatus of the second embodiment whenever used in a method of the first embodiment.

According to a fourth embodiment of the present invention there is provided a photopolymerised dental composition when prepared by the method of the first embodiment.

Detailed Description of the Invention

The photopolymerisable composition for use in the method of the first embodiment may be any polymerisable composition which is capable of being polymerised when irradiated with light. Typically the photopolymerisable composition is a dentally acceptable composition which is known for use in the treatment of dental caries, and includes a resin, photoinitiator and optionally one or more fillers, accelerators and/or inhibitors. Suitable resins are multifunctional acrylic resins, bis/GMA, urethane dimethacrylates, epoxies, EGDMA, oligo dimethacrylates, oligo glycol dimethacrylates, oligo bisphenol A dimethacrylates and urethane methacrylates. Generally, the resin is an acrylic resin or a light-curable glass ionomer cement known in the art.

The photoinitiator may be any substance which is capable of initiating polymerisation of the resin when irradiated with light of an appropriate wavelength. Such photoinitiators are known and include, for example, benzophenone; xanthone; thioxanthone; 2-chlorothioxanthone; camphorquinone; benzils; benzoins and benzoin ethers; phenanthraquinones; quinones; substituted benzophenones such as Mischlers ketone; α,α-dimethoxy-α-phenylacetophenone; α,α-diethoxyacetophenone and 1-phenyl-1,2-propanedione-2-O-benzoyl oxime. Generally, the photoinitiator is camphorquinone, optionally in conjunction with a tertiary amine accelerator.

Suitable fillers for the photopolymerisable composite include fine particles or fibres of glass, precipitated silica particles or fibres, ceramic fibres or particles, metal fibres or particles and polymeric fibres or particles.

Other suitable photopolymerisable composites are disclosed in International Patent Application No. WO90/08799, for example, the disclosure of which is incorporated herein by reference.

It is known that photoinitiators typically absorb light only over a limited range of wavelengths. For example, the absorption spectrum of camphorquinone shows absorption of light substantially only in the range of wavelengths of about 400mm to 500mm. The absorption maxima of other known photoinitiators such as those exemelified herein above are well known or readily ascertainable persons of ordinary skill in the art. In the method and apparatus of the present invention the light-emitting diode light source is selected so as to have an emission wavelength maximum within the range of wavelengths absorbed by the photoinitiator. For example, it has been found that blue light emitting diodes (LEDs) have an emission spectrum which substantially overlaps with the absorption spectrum of camphorquinone. Other types of light emitting diodes, having emission wavelength maxima in the range of wavelengths absorbed by other photoinitiators, and therefore suitable for use with those photoinitiators in a method in accordance with the invention, may be readily selected by persons of ordinary skill in the art, given the teaching herein.

Typically in the first and second embodiments the source of the irradiating light is a plurality of light-emitting diodes, more typically blue light-emitting diodes. Still more

typically the light-emitting diodes have an emission wavelength maximum of about 450nm. Typically, the number of LEDs is selected in order to generate enough light intensity to cure a composite in a time comparable to that required when a conventional tungsten-halide lamp is used in prior art methods. Usually, the number of light-emitting diodes is from 20-1000, more usually from 25-500, still more usually from 40-400 or 50-250, even more usually from 60-200, yet more usually from 75-150 and even more usually still, about 100.

The LEDs can be arranged in any convenient shape or pattern, such as square, rectangular, circular, oval, pentagonal, hexagonal, heptagonal, octagonal, etc. Typically, approximately 100 LEDs are arranged in an hexagonal pattern to fill a roughly circular zone of approximately 50 mm diameter. In this arrangement it is possible to construct a hand-held dental light source with an optical output exceeding 100 mW, as described in more detail below.

The array of LEDs can be connected electrically in series, or in parallel connections of one or more series of strings of one or more LEDs (for example, in 12 strings of nine LEDs to make an array of 108 LEDs or 10 strings of 10 or 15 strings of 8 or 12 strings of 10 or 8 strings of 12, etc). For series connection, the string may be powered by a single stabilised current source regulating in the range 20-100 mA. For parallel strings, the current in each string must be regulated within this range by, for example, using a simple current mirror circuit. The power source for the LEDs may be rectified mains power, a battery, solar cells or any other convenient source capable of supplying sufficient power (approximately 10-15W for an array of 100 LEDs.) Where batteries are used they may be rechargeable or single-use type.

Typically in the method and apparatus of the invention the source occupies an area of several square centimetres. For example, an array of 100 LEDs occupies an area of 50-60 mm diameter. The condenser means in the apparatus of the invention efficiently collects light emitted by the source and delivers it to one end of the light conduit. Typically from 50% to 99.9%, more typically 60% to 90%, still more typically 70% to 80% of the light emitted by the light source is delivered by the condenser means to the proximal end of the light conduit at such an angle that it enters the acceptance zone of the light conduit. For dental applications the light conduit is small enough to fit comfortably inside the mouth and illuminate essentially only the tooth being treated. Alternatively, the method of the first embodiment may comprise directing light from the light source, for example using an apparatus of the second embodiment or other focussing arrangement, onto a photopolymerisable composite for curing it externally to the mouth, the cured composition being bonded to a tooth under treatment by clinical procedures.

The condenser means may typically comprise one or more lenses or lens arrays, one or more diffractive elements, or a solid, hollow or liquid-filled element adapted so that light entering the element at one or more surfaces thereof is totally internally reflected and

concentrated optically before emerging from another surface thereof. Typically when the condenser is a liquid filled element, the liquid has a refractive index sufficiently higher than that of the material from which the hollow element is constructed, that light impinging on the internal surface of the hollow element tends to be totally internally reflected. Suitable liquids for filling such a hollow element include water, aqueous solutions of salts, glycerol, silicones, oils or other dense clear liquids. Typically, the refractive index of such liquids is at least 1.1, more typically at least 1.3, even more typically from about 1.4 to 2.2, still more typically from about 1.5 to 2 or more.

Alternatively, combinations of two or more of these elements may be used. Generally, the profile of the concentrator is optimised to suit collection of light at one of its ends from an extended, divergent source (such as an array of LEDs) and is tapered so as to deliver the light at an opposite end from an aperture whose diameter matches the intended requirement (for example, the illumination of a single tooth). The precise shape of the condenser means depends on the nature of the element (for example diffractive, reflective, refractive) employed, the material of its construction and the size and shape of the light source. Given the teaching herein, however, the design and fabrication of a suitable condenser for any desired apparatus in accordance with the present invention is well within the normal capabilities of a person of ordinary skill in the art.

The condenser means provides optical concentration of light emitted from the light source for delivery to the proximal end of the light conduit, whose diameter is typically from about 3 to about 20 times smaller, more typically from about 4 to 10 times smaller, than that of the light source. In particular, this optical concentration can be accomplished by one or a combination of two or more of the following elements:

a) a moulded, formed, cast, machined or shaped element of suitably tapered form as exemplified in more detail below, consisting of transparent material, with or without a suitable cladding of lower refractive index, which utilises total internal reflection to transfer light from the light source to the smaller diameter of the light conduit;

b) a moulded, formed, cast or shaped element as described for (a), further including a fresnel lens or other refractive element formed into a surface of the condenser onto which light from the light source falls, for the purpose of directing light more efficiently into the condenser;

c) element (a) or (b) above, fabricated from transparent material having a graded refractive index profile from the end adjacent to the light source to the opposite end;

d) a hollow element of suitably tapered form, either air or liquid-filled, which utilises total internal reflection to transfer light from the light source to the smaller diameter of the light conduit;

e) diffractive optical elements arranged in relation to individual elements of the light source so as to direct the light into the proximal end of the light conduit; or

f) one or more replicated microlens arrays arranged in relation to individual LEDs of the light source so as to direct the light into the proximal end of the light conduit, either alone or in conjunction with one or more of elements (a), (b), (c), (d) or (e). Additionally, an element of type (a), (b), (c) or (e) may be metallised on its exterior surface to promote total internal reflection, or an element of type (d) may be metallised on its interior surface.

Generally the condenser, if of type (a) or (c), is convex at the end which receives light from the light source, when viewed from the direction of the light source, so as to provide an initial focus for the light. Alternatively, the light source may be generally concave when viewed from the direction of the condenser, so as to achieve a similar initial focus of the light.

One preferred condenser consists of a machined cast or moulded tapered element made of a transparent material (such as glass or acrylic or other optical grade plastics such as polycarbonate) which utilises refraction at a curved, stepped or Fresnel-cut input surface to direct light from divergent LED sources towards the exit aperture of the condenser, and total internal reflection over a predetermined tapered shape to enhance the collection efficiency. In this form of the condenser, the tapered section extends from a diameter slightly larger than that of the LED array to a diameter of size suitable for the application of the apparatus, typically a dental application, and abuts or merges contiguously with a lightguide of a length sufficient for use in the desired application, scuh as in an oral cavity. Generally, the refractive index of the transparent material from which the condenser is constructed is about 1.5, whence the critical angle of the material is about 41° when the condenser is surrounded by air. The shape of the condenser is then selected so that light entering it impinges on its sides at an angle greater than this value (measured with respect to the normal), typically 50-60°, so that usually 2, 3, or 4 internal reflections occur before most of the light reaches the exit aperture of the condenser.

The light conduit of the apparatus of the invention may be an optical wave-guide generally known in the art and usually consists of a rigid or flexible bundle of optical fibres. Alternatively, a liquid-filled tube with materials of appropriate refractive index can be used to ensure total internal reflection and thus efficiently to transfer the light from the exit aperture of the condenser to an oral cavity. The light conduit alternatively may be a rod of suitable transparent material such as optical grade acrylic, polycarbonate or glass. In one form of the invention, the light conduit may be integral with the condenser means, for example forming a continuation of a tapered end of a solid or hollow element such as described above. The inclusion of the light conduit as a contiguous part of the cast or moulded element improves coupling efficiency by eliminating unnecessary material interfaces and consequent reflection and other losses at the boundaries.

The light conduit of the apparatus may be straight, bent or fitted with an adaptor to suit a range of waveguide accessories generally known for use in dental practice. It will

typically have a substantially constant diameter throughout its length, but may alternatively be of another shape, for example tapered from its proximal end to its distal end.

In the apparatus of the second embodiment, the distal end of the light conduit is typically adapted to be placed in close proximity with a polymerisable dental composition whose polymerisation is to be photoinitiated by light from the source. More typically, the distal end of the light conduit has a diameter of from 5 mm to 15 mm and is adapted to be positioned close to the unpolymerised dental composition, for example in a tooth to be filled.

In another form of the apparatus of the invention, the condenser and light conduit are hollow and can, for example, be fabricated from electro-formed nickel. In this form, the weight of the condenser is typically reduced compared to solid condensers, making hand-held operation of the apparatus more comfortable for the operator.

An apparatus in accordance with the second embodiment of the invention is typically used by dentists to carry out, in short succession, a series of 30-60 second exposures within the space of a few minutes (while the dental cavity is filled with composite and successive layers cured), following by a non-usage period of ten minutes to several hours (corresponding to the change from one patient to the next).

With such a pattern of operation, the need for any forced cooling of the close-packed LED array may be eliminated by mounting the LEDs on a heat-sink which has sufficient thermal mass to allow the LEDs to be over-driven for a period of up to a few minutes without exceeding the temperature rating of the semi-conductor materials of the LEDs. For example the LEDs may be mounted on a circuit board in such a way that the electrical connectors thereto extend beyond the rear of the circuit board and are encapsulated in a relatively large mass of electrically insulating, thermally conductive high specific heat epoxy material such as, for example, epoxy potting resin containing finely divided ceramic particles. The epoxy material may be enclosed within the apparatus or it may extend to the outer surface of the apparatus so that any accumulated heat can dissipate to the ambient air. The epoxy material can also be connected thermally to an optional internal or external conventional finned heatsink.

Alternatively, the LEDs may be immersed within the liquid of a liquid-filled tapered hollow condenser, with the circuit board on which the LEDs are mounted forming part of the sealed enclosure of the liquid. The liquid-filled enclosure then fills the dual roles of optical concentrator and thermal heat sink.

In the method of the first embodiment the step of irradiating the composition may comprise irradiating the composition with light uninterruptedly (that is, with a continuous stream of light) or irradiating the composition with pulsed light.

It is known that increasing the current to a light source results in a higher instantaneous optical flux and that the curing rate of composites has a quadratic

dependence on the light intensity. Because a current higher than the normal continuous value can only be applied to a LED for a short period of time, increased instantaneous light intensity is obtained at the cost of reduced duty cycle. Therefore, if increased instantaneous light intensity is to be obtained from a light source, it must be pulsed.

An incandescent source cannot be rapidly pulsed because of the difficulties in heating and cooling the thermal element, and operating a higher current rapidly reduces lamp lifetime. By contrast, an LED source is easily operated in an optional pulsed mode.

An advantage of a pulsed source in dental applications is that over a significant range of duty factors, lower average intensity (which means lower input power) can be used without significant degradation of the rate of cure of a photocurable polymer. When the LED source is operated in a pulsed mode and without exceeding the specified operational limits of the apparatus, effectively the same cure rate may be obtained over a significant range of duty factors. For example, it is possible to obtain a 5 mm depth of cure in a 5 mm diameter sample of composite with either: (i) a 40 second exposure to light from a 108 element LED array operated at a continuous 30mA per LED, or (ii) a 48 second exposure to light from the same array when operated at 40mA per diode and a 60% duty cycle.

In the case of the latter, there is a 25% reduction in the power consumption and a 25% reduction in the total energy dose of the light. These translate to:

a further reduction in the electrical power and cooling requirements of the system, thereby reducing size and improving the between-charge lifetimes of battery-operated versions; and

a further reduction in heat buildup and consequent internal stress in the composite during curing.

Brief Description of the Drawings

Figure 1 represents the emission spectrum of a typical blue light-emitting diode, superimposed on the absorption spectrum of camphorquinone.

Figure 2 is a diagrammatic cross-section of an apparatus in accordance with the second embodiment of the invention.

Figure 3 is a diagrammatic cross-section of an alternative LED array and heatsink assembly for use in an apparatus in accordance with the invention.

Figure 4 is a diagrammatic cross-section of a LED array/condenser assembly for use in an apparatus in accordance with the invention.

Best Method and Other Methods for Carrying Out the Invention

Figure 1 represents the emission spectrum of a typical blue light-emitting diode (100), superimposed on the absorption spectrum of camphorquinone (110). It will be seen that the emission maximum of the blue light-emitting diode (120) occurs within the range of wavelengths of light absorbed by camphorquinone, and that a very substantial

amount of the light emitted by the blue light-emitting diode is capable of being absorbed by camphorquinone.

Figure 2 shows a cross-section of typical version of a complete apparatus in accordance with the invention suitable for dental use.

As seen in Figure 2, apparatus 200 comprises body 210 and handle 215. Body 210 consists of nose section 211, centre section 212 and rear section 213. Nose section 212 is generally hollow and tapered, and has an opening at its narrower end which houses connector 218 in which is mounted proximal end 221 of light conduit 220. Connector 218 also supports an end of condenser 230 and holds the end of condenser 230 in close proximity to proximal end 221 of light conduit 220. Condenser 230 is of generally tapering shape as shown in Figure 2 and is symmetrical about its longitudinal axis. The wider part of condenser 230 is mounted mainly within body centre section 212 and is held in place by mounting rings 231, 232. Mounted towards the rear end of centre section 212 is an array of blue LEDs 240 mounted on circuit board 245, electrical connections 241 to LEDs 240 being embedded in epoxy resin heatsink 250. Control circuit board 260, containing the electrical componentry for controlling the LEDs, including pulsing them if desired, is mounted in handle 215 and is electrically connected to switch 265 and timing control 270. Timing control 270 protrudes from the rear of body rear section 213 and includes a rotatable knob, rotation of which permits an operator of apparatus 200 to adjust the time of irradiation of a dental cavity with light from apparatus 200. Power cable 270, connected to external power source 280 (which may be a mains plugpack or battery) enters handle 215 through a hole in its bottom end and is held in place by cable clamp 275. Wires (not shown) connect power cable 270 to control circuit board 260. Light conduit 220 is elongated and has a bend formed adjacent distal end 222.

In use, after a photoplymerisable dental composition has been introduced into a tooth having a cavity to be filled, distal end 222 of light conduit 220 of apparatus 200 is brought adjacent to the surface of the photoplymerisable composition in the cavity. The operator then selects, using timing control 270, the time of irradiation of the composite in the dental cavity, and switch 265 is operated. Switch 265 typically has three positions, namely "off", "pulsed" and "continuous". When the "pulsed" position on 265 is selected, a pulsed electrical current is provided to LEDs 240 and LEDs 240 emit pulsed light. Similarly, when the "continuous" position is selected using switch 265, a continuous stream of light is emitted from LEDs 240. Light emitted by LEDs 240 is collected by condenser 230 and is concentrated therein and conveyed to proximal end 221 of light conduit 220 whereby it is conveyed to distal end 222 of light conduit 220 and illuminates the dental composition in the tooth.

Figure 3 provides a diagrammatic cross-section of an alternative assembly of LEDs, circuit board and heat sink for use in an apparatus of the invention. Referring to Figure 3, assembly 300 comprises an array of LEDs 340 mounted on circuit board 345, electrical

connections 341 to LEDs 340 extending into and being embedded in epoxy resin heatsink 350. Connections 341 are not trimmed to the level of circuit board 345 after being soldered in place and may include an optional metallic sleeve 342, added during the soldering process, to improve thermal transfer between LEDs 340 and resin 350 and to increase the effective thermal mass of connectors 341.

A conventional finned heatsink 355 is embedded on the face of epoxy resin heatsink 350 remote from circuit board 345 in order to improve the dissipation of heat from assembly 300. Assembly 300 is mounted in proximity to condenser 330 as generally shown in Figure 2.

Figure 4 provides a diagrammatic cross-section of a further alternative arrangement in which an array of LEDs is mounted within a high refractive index liquid contained within a hollow condenser. Referring to Figure 4, condenser/source assembly 400 comprises hollow condenser shell 410 of predefined shape containing liquid 420 having a higher refractive index than the material of shell 410 to provide a low internal critical angle and thus facilitate total internal reflection of light within shell 410. Narrow end 415 of shell 410 is sealed to a light conduit (seal and conduit not shown) and the other end of shell 410 is closed by printed circuit board 430 on which is mounted array 440 of LEDs. Seal 450 around the circumference of shell 410 prevents loss of liquid 420 between shell 410 and circuit board 430. Heatsink 460 such as generally shown in Figure 2 or Figure 3 may optionally be included in contact with the exposed face of circuit board 430.

Example

The following is an example of a photopolymerisable dental composition which may be polymerised by the method of the invention and/or using an apparatus of the invention:

Bisphenol A di(glycidyl methacrylate)	67.0% w/w
2-hydroxyethyl methacrylate	32.64% w/w
Camphorquinone	0.15% w/w
N,N,3,5-tetramethylaniline	0.16% w/w
Butylated hydroxy toluene	0.05% w/w

This composition may be cured by irradiating it with light having a maximum intensity at about 450 nm and emitted from an array of blue light emitting diodes.

The method and apparatus of the present invention provide a number of advantages in comparison with prior art devices, for example the following.

A. A close correspondence between the source emission spectrum and the photoinitiator absorption spectrum means that little of the output light from the light source is wasted. Thus, the same active light dose can be provided to a photopolymerisable composite in comparison to prior art methods, for lower optical power, reduced overall brightness, reduced heating, lower electrical input and reduced potential for eye damage. The close correspondence between the source emission spectrum and the photoinitiator absorption

spectrum also facilitates optimal conversion of the photopolymerisable composite and thus results in the cured composite having superior mechanical properties in comparison to composites cured by methods of the prior art.

B. No optical filters, which are inefficient, are needed in the apparatus of the present invention. There is no delivery to the target of unwanted and useless wavelengths which leak through the filters; this means that there is no thermal stress on the composite during curing and results in better mechanical properties for the more efficiently cured material for a given dose, and a better fit to the dental cavity. Furthermore, with no spectral filters to degrade as they age, there is no possibility of degraded spectral quality over the lifetime of the apparatus.

C. LEDs are more efficient sources of light than conventional lamps. This means that no cooling fan is needed in the apparatus of the invention, and the power supply can be smaller than that needed for tungsten halide lamps. As a result, the apparatus of the invention can be hermetically sealed and thus easily sterilised.

D. Higher electrical efficiency means that battery operation of an apparatus according to the invention is possible, thus eliminating the need for trailing cords and making the apparatus more portable and convenient to use compared to mains operated devices of the prior art.

E. The operating lifetime of the light source in the method and apparatus of the invention is measured in thousands rather than hundreds of hours, and the light output of the light source is stable over the operating lifetime of the source.

F. There is no unwanted UV radiation from the source and thus there is no UV hazard to the operator or patient, nor any need for a viewing shield for the operator.

G. There is no radiation at unwanted visible or infra-red wavelengths so that there is a substantial reduction in the overall source intensity needed to achieve similar curing results. Lower overall intensity also makes viewing the treatment more comfortable for the operator.

CLAIMS:

1. A method for initiating the polymerisation of a photopolymerisable dental composition comprising a photoinitiator capable of initiating said polymerisation when irradiated with light having a wavelength between a lower wavelength and an upper wavelength, which method comprises the step of irradiating said composition with light emitted from a light-emitting diode source having an emission wavelength maximum between said lower wavelength and said upper wavelength.

2. A method according to claim 1 wherein said light-emitting diode source comprises a plurality of light-emitting diodes.

3. A method according to claim 2 wherein said light-emitting diodes are blue light-emitting diodes.

4. A method according to claim 3 wherein said light-emitting diodes have an emission wavelength maximum of about 450nm.

5. A method according to claim 1 wherein said step of irradiating said composition comprises irradiating said composition with pulsed light.

6. A method according to claim 1, wherein said photoinitiator is camphorquinone.

7. A polymerised photopolymerisable dental composition whenever prepared by the method of any one of claims 1-6.

8. An apparatus for irradiating a photopolymerisable dental composite comprising a light-emitting diode source, a light conduit having a proximal end and a distal end, and condenser means operatively associated with said source and said light conduit for directing light emitted by said source onto said proximal end of said light conduit.

9. An apparatus according to claim 8 wherein said light-emitting diode source comprises a plurality of light-emitting diodes.

10. An apparatus according to claim 9 wherein said light-emitting diode source comprises from 20 to 500 light-emitting diodes.

11. An apparatus according to claim 10 wherein said light-emitting diodes are blue light-emitting diodes.

12. An apparatus according to claim 8 wherein said condenser means is selected from the group consisting of:

one or more lenses or lens arrays;

one or more diffractive elements;

a solid, hollow or liquid-filled element adapted so that light entering the element at one or more surfaces thereof is totally internally reflected and concentrated optically before emerging from another surface thereof; and

a combination of two or more thereof.

13. An apparatus according to claim 8 wherein said condenser is a hollow liquid-filled element, said liquid having a refractive index sufficiently higher than that of material from which said hollow element is constructed, for light impinging on an internal surface of said hollow element to be totally internally reflected.

14. An apparatus according to claim 13 wherein said light-emitting diode source is immersed in said liquid.

15. An apparatus according to claim 8, wherein said condenser is a tapered element which utilises total internal reflection to transfer light from said light source to said proximal end of said light conduit.

16. An apparatus according to claim 15, wherein said tapered element is a moulded, formed, cast, machined or shaped element consisting of a transparent material.

17. An apparatus according to claim 15, wherein said tapered element is hollow and is filled with air or a liquid.

18. An apparatus according to claims 16 or 17, wherein said condenser means further comprises a refractive element formed into a surface of said condenser onto which light from said light-emitting diode source falls.

19. An apparatus according to claim 8, wherein said condenser means is fabricated from transparent material having a graded refractive index profile from an end adjacent said light source to an end adjacent said proximal end of said light conduit.

20. An apparatus according to claim 8, wherein said light conduit is a bundle of optical fibres.

21. An apparatus according to claim 8, wherein said light conduit is a liquid-filled tube.

22. An apparatus according to claim 8, wherein said distal end is adapted to be placed in close proximity with a polymerisable dental composition whose polymerisation is to be photoinitiated by light from said source.

23. An apparatus according to claim 22, wherein said polymerisable dental composition is in a tooth.

24. An apparatus according to claim 8, whenever used to initiate the polymerisation of a photopolymerisable dental composition by a method according to any one of claims 1-6.

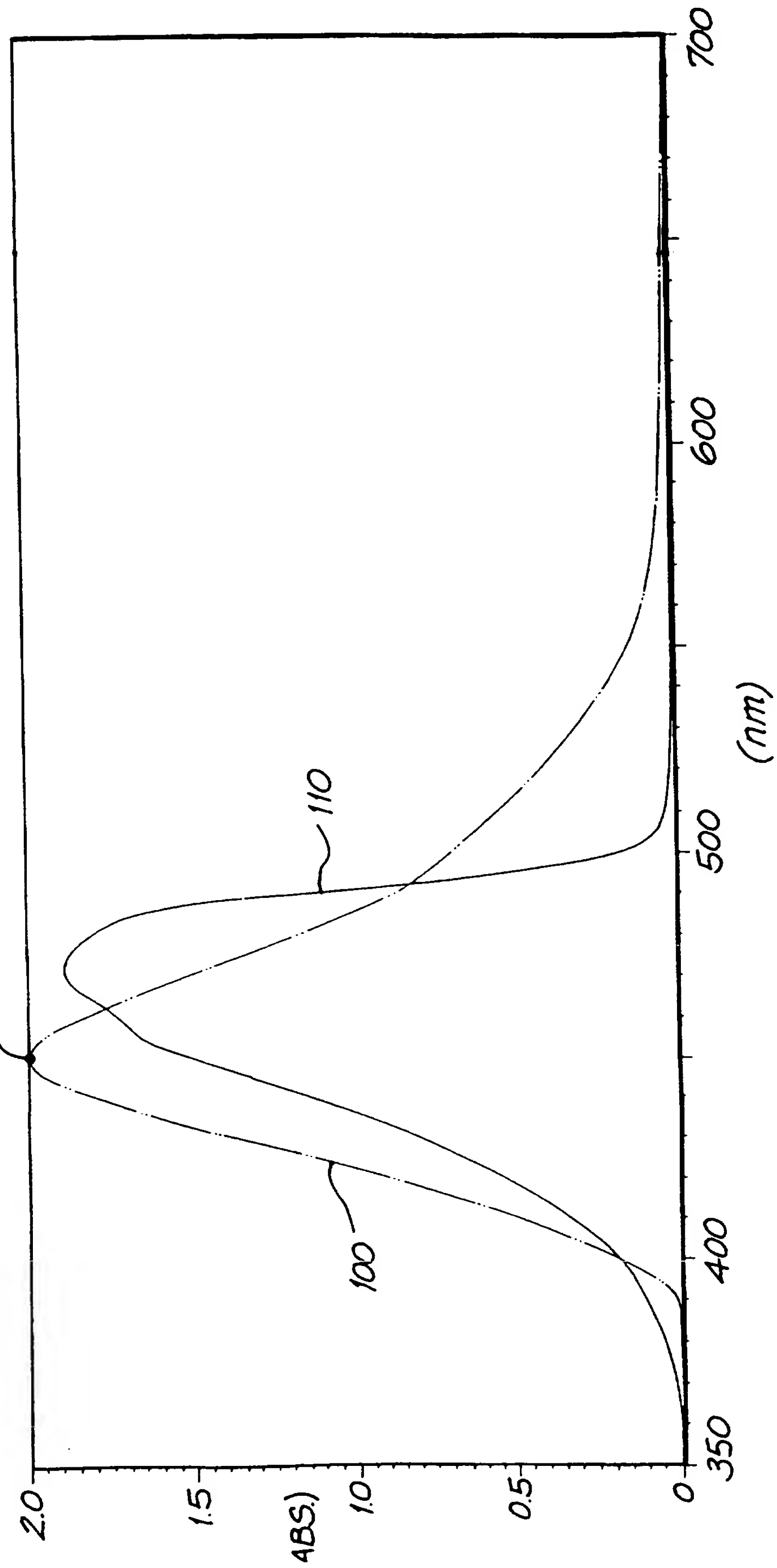

FIG. 1

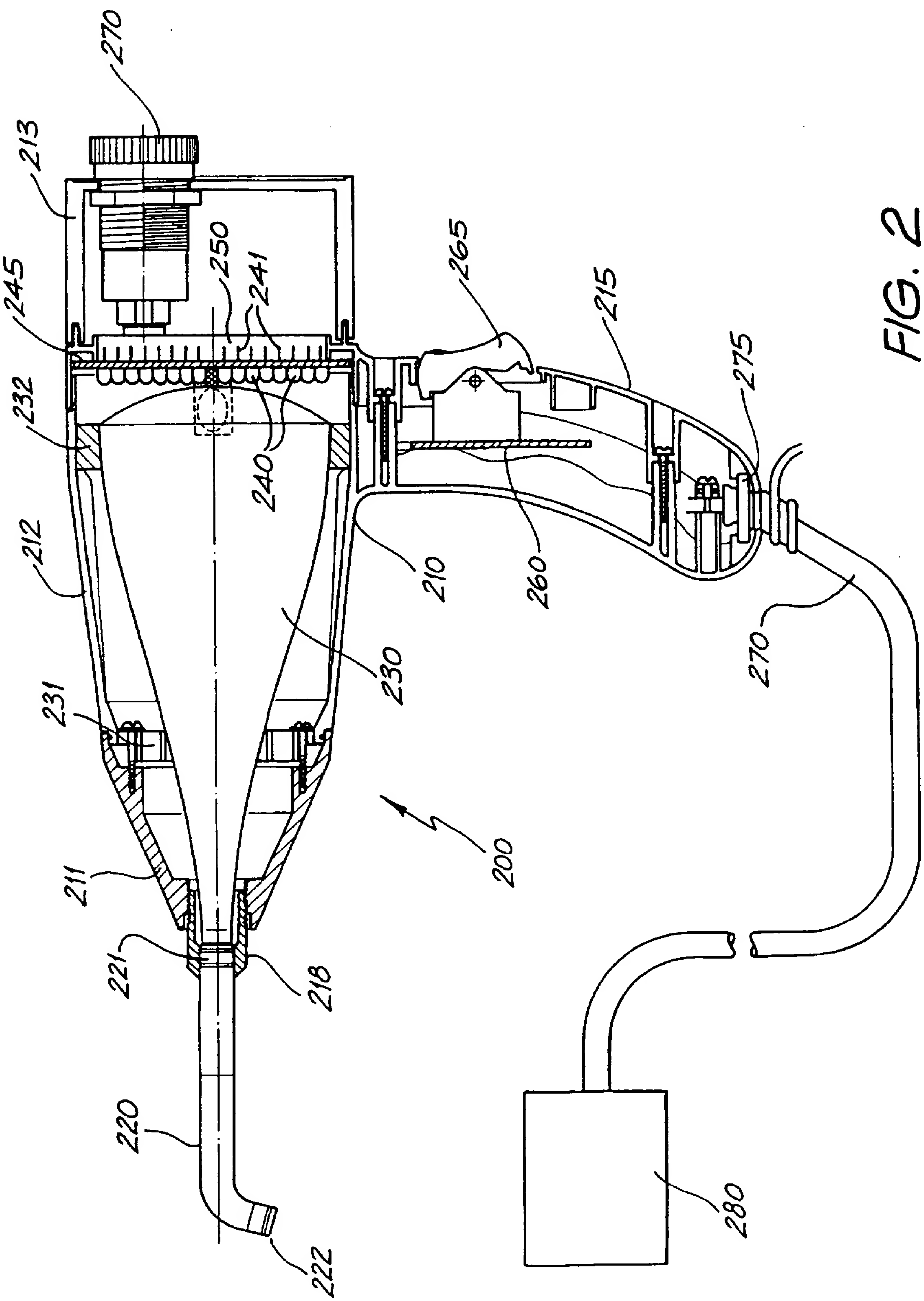
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FIG. 2

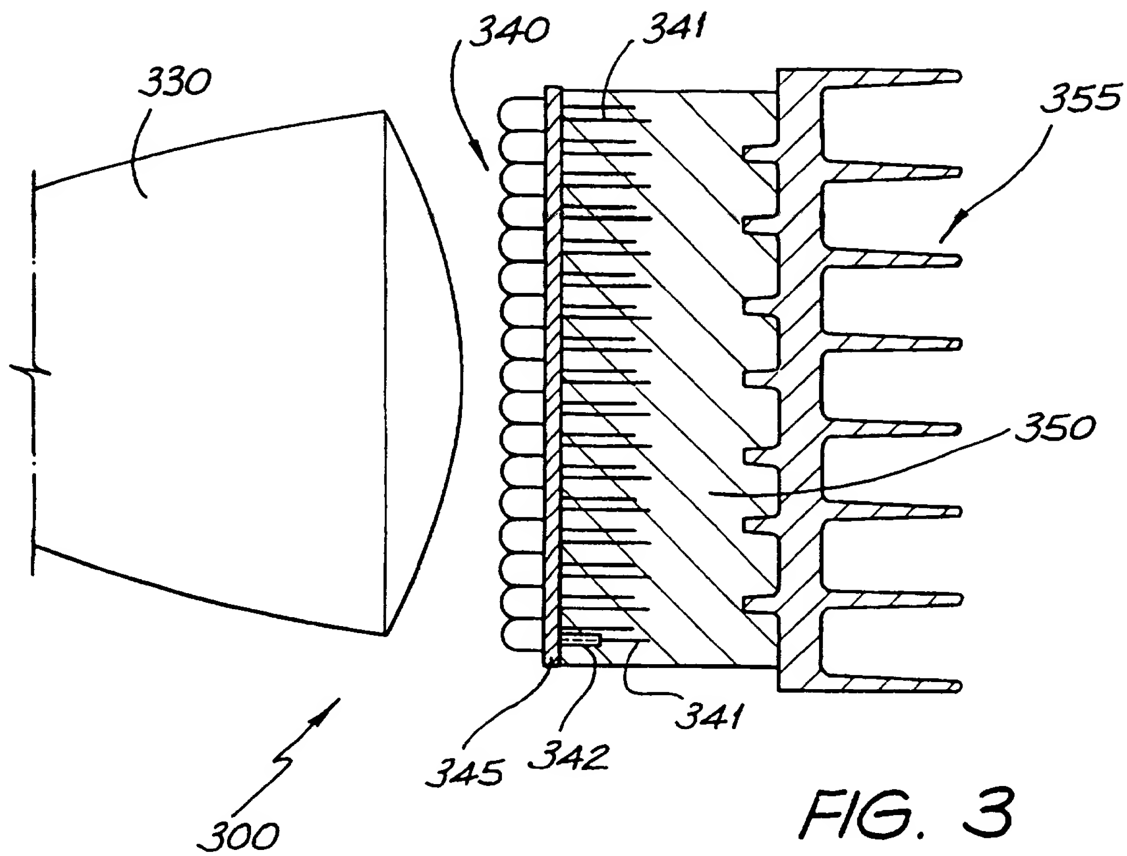
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FIG. 3

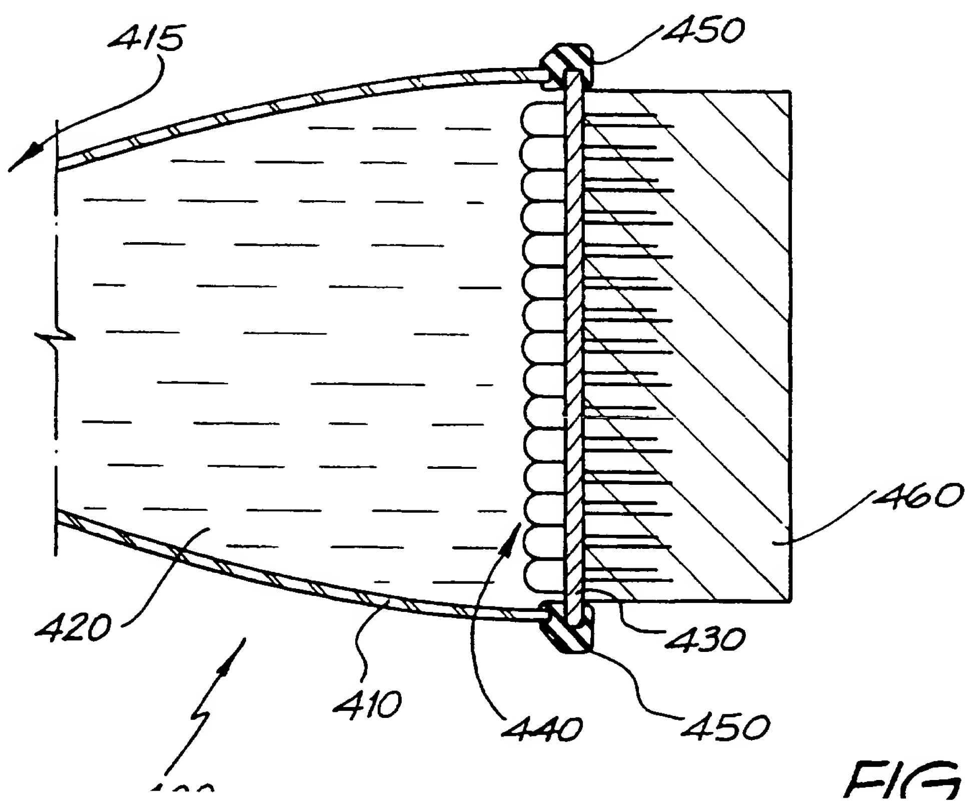
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FIG 4

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/AU 97/00207

A. CLASSIFICATION OF SUBJECT MATTER

Int Cl^6: A61C 13/15

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A61C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
A61C 5/04, 3/00, 13/14, 13/15

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Derwent
Japio
Medline

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 5420768A (KENNEDY) 30 May 1995 entire document	1-24 1-24
X	Patent Abstracts of Japan, JP 07-240536 A (SHIMADZU CORP) 12 September 1995 abstract and figure	1-24
P,X	Patent Abstracts of Japan, JP 08-141001 A (OSADA RESEARCH INSTITUTE LTD) 4 June 1996 abstract	1-24

☐ Further documents are listed in the continuation of Box C ☐ See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
5 may 1997	16.05.97

Name and mailing address of the ISA/AU
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MATTHEW FORWARD

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/AU 97/00207

C (Continuation)	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	Patent Abstracts of Japan, JP 09-010238 A (NAGATA CHUO KENKYUSHO KK) 14 January 1997 abstract	1-24
Y	DE 3411996 A1 (KULZER & CO) 3 October 1985 see figures	1-24
Y	AU 29350/89 A (PETZ) 14 June 1990 abstract and figures	1-24
Y	US 5198678 A (OPPAWSKY) 30 March 1993 entire document	1-24

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/AU 97/00207

Box 1 Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. [ ] Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. [ ] Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. [ ] Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Claims 1 and 8 lack unity 'a posteriori' in view of the prior art cited in this report. Further the apparatus of claim 8 and method of claim 1 are not restricted to the same or similar scope.

1. [ ] As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims
2. [X] As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. [ ] As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. [ ] No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest [ ] The additional search fees were accompanied by the applicant's protest.

[ ] No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International Application No.
PCT/AU 97/00207

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
US	5420768	AU	77378/94	WO	9507731		
JP	7240536	NONE					
JP	8141001	NONE					
JP	9010238	NONE					
DE	3411996	NONE					
AU	29350/89	DE	3840984	EP	397732	WO	9006092
US	5198678	EP	474976	JP	5184603		
							END OF ANNEX